

# PATENT SPECIFICATION

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(72) Inventors CHRISTOS PAPANTONIOU and QUINTINO  
GAETANI



## (54) COMPOSITIONS FOR APPLICATION TO THE HAIR BASED ON TWO-BLOCK AND THREE-BLOCK COPOLYMERS

(71) We, L'OREAL, a French Body Corporate of 14, Rue Royale, 75008 Paris, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to compositions for hair, in particular for lacquers and wave-setting lotions, which contain block copolymers as the resin.

We have already proposed the use of numerous synthetic polymers for producing such types of composition. We have, in particular, proposed the use of certain heterogeneous polymers as well as the use of certain homogeneous polymers.

We have now found that it is possible to produce excellent compositions for hair, especially lacquers and wave-setting lotions, by using other types of polymers, namely block polymers and more particularly two-block or three-block polymers of a particular type.

As will be seen later, these polymers are of very great interest because it is possible to obtain polymers having different properties merely by varying the nature of the blocks. This feature of the block polymers is of great advantage especially for the production of compositions in the form of lacquers or wave-setting lotions because, as is known, some are produced in aqueous or aqueous alcoholic solution and others exclusively in alcoholic solution.

It is well known that the different monomers involved in the formation of copolymers can behave in different ways in leading to the formation of the polymer chain; in general terms the polymerisation processes make it possible to direct matters so that one or another type of polymer is obtained. In particular, with a well-defined polymerisation process it is possible to obtain copolymers in which the monomer units are grouped according to type, these groups being referred to as a "sequence" or a "block". Such copolymers are generally called block copolymers.

Block polymers are generally binary polymers comprising two or three blocks each consisting of identical monomers. The copolymers used in the compositions of the present invention are two-block or three-block copolymers, that is to say the distribution of the monomer units or blocks in the polymer chain can be represented schematically as follows:

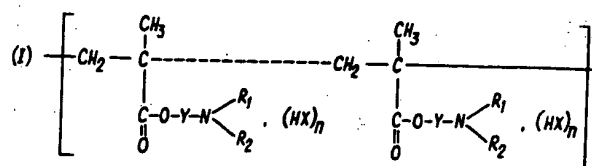
XXX ... XXXZZZ ... ZZZ (1)

or as follows:

XXX ... XXXZZZ ... ZZZXXX ... XXX (2)

According to the present invention there is provided a composition suitable for application to the hair, in particular a lacquer or wave-setting lotion, which is oil-free

and contains, in an acceptable cosmetic vehicle, at least one two-block or three-block copolymer containing, firstly, at least one block (A) corresponding to the formula:



in which:

Y represents a saturated hydrocarbon chain of 2 to 4 carbon atoms, or a hydrocarbon chain of 2 to 4 carbon atoms, interrupted by one or more hetero-atoms such as sulphur or oxygen;

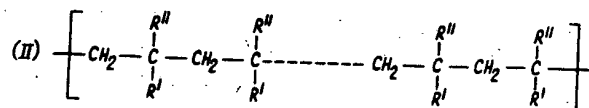
R<sub>1</sub> and R<sub>2</sub>, which may be identical or different, each represents an alkyl radical of 1 to 4 carbon atoms;

n is 0 or 1,

HX represents an inorganic or organic acid chosen from hydrochloric acid, hydrobromic acid, lactic acid and acetic acid,

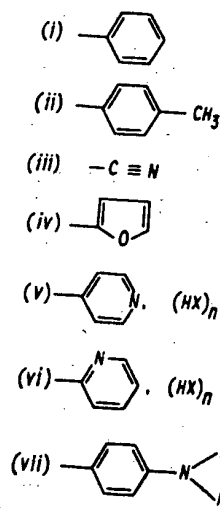
and, if any n is 0, the corresponding tertiary amine group is optionally quaternised, and, secondly, at least one block (B) resulting from the polymerisation of an anionically polymerisable monomer.

Preferably, the block (B) has the following formula:

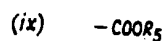


in which:

R' is chosen from



with R'' representing  
a hydrogen atom



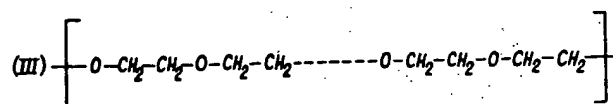
with R'' representing  
a methyl radical

which may be neutralised or salified as hereinafter indicated

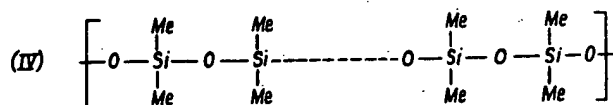
in which  $R_1$ ,  $R_2$ ,  $n$  and  $HX$  are as defined above,  $R_3$  represents an alkyl radical of 6 to 18 carbon atoms,  $R_4$  represents a methyl or ethyl radical and  $R_5$  represents alkyl radical of 1 to 18 carbon atoms.

According to a preferred embodiment, the radicals  $R'$  are of formula (i) or (ix).

Alternatively, the block (B) results from the polymerisation of ethylene oxide and can be represented by the following formula:



Again, the block (B) can result from the polymerisation of hexamethyl-cyclo-trisioxane or octamethyl-cyclo-tetrasiloxane, and can be represented by the following formula:



Referring to the schematic formulae (1) and (2) above, the two-block and three-block polymers used according to the invention can thus assume the following form:

- (i) AAA—BBB
- (ii) AAA—BBB—AAA or
- (iii) BBB—AAA—BBB

in which the block (or blocks) A correspond to those of formula I and the block (or blocks) B correspond to those of formula II, III or IV.

Amongst the monomers which can lead to the formation of the blocks A of formula I there may be mentioned the following: 2 - (N,N - dimethylamino) - ethyl methacrylate, 2 - (N,N - diethylamino) - ethyl methacrylate, 2 - [2' - (N,N - dimethylamino)ethoxy] - ethyl methacrylate and 2 - [2' - (N,N - diethylamino)ethoxy] - ethyl methacrylate.

Amongst the monomers which can lead to the formation of blocks B of formula II there may be mentioned the following: styrene, 4 - methyl - styrene, 2 - vinyl - pyridine, its hydrochloride and its lactate, 4 - vinyl - pyridine, its hydrochloride and its lactate, para - dimethylaminostyrene, its hydrochloride and its lactate, methyl methacrylate, ethyl methacrylate, butyl methacrylate, hexyl methacrylate, octyl methacrylate, lauryl methacrylate and stearyl methacrylate, methacrylonitrile, 2 - vinyl-furane and N - methyl - N - lauryl - methacrylamide.

If  $R'$  in the block B of formula II represents a carboxylic acid group, this group can be neutralised with an inorganic or organic base such as ammonia, monoethanolamine, diethanolamine, triethanolamine, the iso - propanolamines, morpholine, 2-amino - 2 - methyl - 1 - propanol and 2 - amino - 2 - methyl 1,3 - propanediol, or be salified in the form of a sodium, potassium or magnesium salt.

In a preferred variant of the invention the tertiary amine groups of the blocks A of formula I ( $n$  being equal to zero) can be quaternised by means of a quaternising agent for example dimethyl sulphate, ethyl bromide or  $\beta$ -bromo-ethanol.

The percentage of the quaternised tertiary amine groups can vary from 0 to 100%, the degree of quaternisation being chosen in accordance with the intended use of the block polymer.

Equally, as is shown by formula I (with  $n=1$ ), a part or all of the tertiary amine groups of the blocks A of the formula I can be salified by an inorganic or organic acid.

As in the case of the quaternised tertiary amine groups, the percentage of salified groups can vary from 0 to 100%.

Thus, lightly quaternised or salified block polymers are preferably used in aerosol lacquers, whilst more highly quaternised or salified block polymers are preferably used in aqueous or aqueous-alcoholic wave-setting lotions.

The molecular weights of the two-block and three-block polymers used according to the present invention can range within wide limits. They are generally fixed in accordance with their intended use, for example as lacquers or wave-setting lotions.

The two-block and three-block polymers according to the present invention

generally have a molecular weight of from 1,000 to 1,000,000, but preferably from 2,000 to 300,000.

As indicated above, the compositions according to the invention can be in various forms and especially in the form of wave-setting lotions, in the form of lacquers or in the form of treatment compositions.

By way of example, an aerosol hair lacquer can be produced by packaging, in an aerosol container, from 0.2 to 5% by weight of the block polymer, from 0 to 35% and preferably from 0 to 25% by weight of an alcohol and from 60 to 99.8% by weight of a liquefied propellant gas under pressure, such as dichlorodifluoromethane, trichlorofluoromethane or a mixture thereof.

Preferably, ethyl alcohol or isopropyl alcohol is used as the alcohol. When no alcohol is used, the propellant gas (or gases) is the sole cosmetic vehicle present in the lacquer described above.

A wave-setting lotion according to the invention can be produced, for example, by introducing from 0.2 to 10% by weight of the block co-polymer into an aqueous or aqueous-alcoholic solution, having an alcohol content of 0 to 60%.

The cosmetic compositions according to the invention can also contain conventional cosmetic adjuvants such as perfumes, dyestuffs, preservatives, plasticisers, thickeners, anionic, cationic or non-ionic surface active agents, silicones for improving the gloss or other cosmetic resins.

The excellent cosmetic properties of the compositions according to the invention are largely due to the presence of at least one block of the formula I in the two-block and three-block polymers.

In fact, the comparative experiments which we have carried out make it possible to demonstrate that if this block of formula I was replaced by other blocks of a different structure, the block copolymers obtained could generally not be used in compositions for hair and especially in lacquers and wave-setting lotions, because of certain properties incompatible with these types of composition.

The two-block and three-block polymers used according to the invention not only have excellent solubility and stability in vehicles for lacquers and wave-setting lotions, but are also insensitive, or only very slightly sensitive, to moisture, which makes it possible to avoid rendering the head of hair sticky and tacky, and form a flexible film over the hair; this film makes the hair pleasant to the touch, and is easily removable by simple brushing or combing.

The present invention also provides a process for setting the head of hair, which process consists of applying a sufficient amount of a composition according to the invention, rolling up the hair on wave-setting rollers and drying the head of hair by external application of heat for a period of, for example, 3 to 20 minutes.

According to a particular embodiment of this process, the composition is applied immediately after rinsing the hair which has been shampooed.

Though the process for the preparation of the block polymers is known, we will summarise the principal stages leading to their formation.

These polymerisation reactions are preferably initiated by so-called "anionic" initiators, which are generally metals belonging to the first group of the periodic table of the elements, such as lithium, sodium and potassium or organometallic compounds of these metals.

For example, there may be mentioned compounds such as diphenylmethyl - sodium, fluorenyl - lithium, fluorenyl - sodium, naphthalene - sodium, naphthalene - potassium, naphthalene - lithium, tetraphenyl - disodio - butane and phenylisopropyl - potassium.

In fact, the choice of the polymerisation initiators is very important because it makes it possible to decide the structure of the block polymer. Thus, naphthalene-sodium makes it possible to direct the polymerisation towards the production of a "three-block" copolymer. In contrast, phenylisopropyl - potassium or diphenylmethyl-sodium make it possible to direct the polymerisation towards the production of a "two-block" polymer.

These polymerisation reactions leading to the formation of block polymers take place in aprotic solvents such as benzene, tetrahydrofuran and toluene.

In general terms, block polymers are obtained as follows. First, a solution of the initiator in the chosen solvent is prepared; then, one of the monomers which is to produce one of the two blocks is added, and after polymerisation of this monomer, the second monomer, which is to lead to the formation of the other block, is added.

After the end of the polymerisation, the block polymer can be deactivated by means of a few drops of aprotic solvent, such as methanol.

In general terms, the reaction leading to the formation of these block polymers is carried out at a temperature of about  $-70^{\circ}\text{C}$ . These polymerisation reactions can

obviously not be carried out with monomers containing mobile hydrogens; such monomers can be, for example, acids, amides which are unsubstituted at the nitrogen, alcohols and compounds containing hydrogens in  $\alpha$ -positions to a carbonyl group.

Consequently, if it is desired to obtain block polymers containing acid groups in one of the blocks, it is necessary to start from monomers which can ultimately lead to the formation of this type of group by chemical reaction. For this purpose it is possible, for example, to start from monomers which possess an ester group. In effect, it is possible to obtain the corresponding acids by hydrolysis.

This type of procedure can be employed if it is desired to obtain blocks consisting of methacrylic acid radicals.

The following Examples further illustrate the present invention; Examples 1 to 23 illustrate the preparation of block polymers used in the cosmetic compositions.

#### PREPARATION EXAMPLES.

##### Two-block copolymers

Examples 1—8.

##### EXAMPLE 1.

Preparation of a polymer from lauryl methacrylate and 2 - N,N - dimethylamino-ethyl methacrylate

2 litres of anhydrous distilled tetrahydrofuran are introduced into a 4 litre flask equipped with a mechanical stirrer, a dropping funnel, a nitrogen inlet tube, a dip tube by means of which samples of reaction mixture can be taken, and thermometer. The flask is then cooled to a temperature of  $-60^{\circ}\text{C}$  by means of a solid carbon dioxide/methanol mixture.

The entire apparatus is placed under an atmosphere of nitrogen which has been carefully purified by heating to  $400^{\circ}\text{C}$  in the presence of copper foil, the stream of nitrogen is also purified by passing over anhydrous potassium hydroxide and over anhydrous magnesium perchlorate.

12.5 ml of a solution of diphenylmethyl - sodium in tetrahydrofuran (0.8 mol per litre) are added dropwise, whilst stirring, from the dropping funnel, and 100 g of pure lauryl methacrylate are then added over the course of 15 minutes whilst continuing the stirring.

After stirring, 100 g of 2 - N,N - dimethylamino - ethyl methacrylate are added, again over the course of 15 minutes, at the same temperature ( $-60^{\circ}\text{C}$ ).

The temperature rises slightly and when the exothermicity of the polymerisation has subsided, the two-block polymer, the two blocks of which consist of poly(lauryl methacrylate) and poly(2 - N,N - dimethylamino - ethyl methacrylate), is deactivated. In general, this last stage is carried out by means of a few drops of methanol. The solution then becomes practically colourless, the tetrahydrofuran is distilled and the residual polymer is dissolved in chloroform and then precipitated by means of petroleum ether. After twice dissolving the polymer in chloroform and twice precipitating it in petroleum ether, the polymer is dried under reduced pressure.

The anticipated two-block polymer is thus obtained in a yield of 80%.

Elementary analysis shows that the polymer consists of 45% of poly(2 - dimethylamino - ethyl methacrylate) and of 55% of poly(lauryl methacrylate) by weight.

The calculated average molecular weight in toluene was 80,000.

This two-block polymer is soluble in an 11/12 Freon mixture (60/40). It is furthermore soluble in absolute alcohol.

This two-block polymer can be quaternised with dimethyl sulphate and the polymer thus obtained is also soluble in the Freons and in absolute alcohol, as well as in a 50/50 alcohol-water mixture. ["Freon" is a Registered Trade Mark.]

##### Examples 2—8 (see Table I)

The two-block polymers shown in Table I were prepared in accordance with the same procedure as that described above for Example 1.

##### Three-block copolymers

Examples 9—12 (see Table II)

The three-block polymers shown in Table II were prepared in accordance with the same procedure as that described above for Example 1.

##### Quaternised or salified copolymers

##### Example 13.

200 g of anhydrous distilled tetrahydrofuran and 40 g of block polymer obtained according to Example 2 are introduced into a 500 ml flask. After the copolymer has

dissolved completely, 3.2 g of distilled dimethyl sulphate are introduced and the solution is stirred for 24 hours at ambient temperature. Tetrahydrofurane is then distilled under reduced pressure.

5 This gives, in a yield of 95%, a block polymer consisting of 27.9% of hexyl methacrylate, 55.6% of 2 - N,N - dimethylamino - ethyl methacrylate and 16.5% of 2 - N,N - dimethylamino - ethyl methacrylate quaternised with dimethyl sulphate. 5

Examples 14—21 (see Table III)

The quaternised polymers shown in Table III were prepared in accordance with the same procedure as that described above for Example 13.

Examples 22 and 23 (see Table III)

10 The salified polymers were also prepared in accordance with the same procedure as that described in Example 13 above. 10

In Table I which follows:

The catalysts used are the following:

- 15 a) diphenylmethyl-sodium  
b) phenylisopropyl-potassium 15

The solvents in which it was possible to measure the number-average molecular weight were the following:

- 20 c) toluene  
d) cyclohexanone. 20

\* The ethylene oxide is introduced by bubbling it through the mixture at 60°C for 4 hours, and the living polymer is then deactivated with water.

\*\* After introducing the octamethylcyclotetrasiloxane, the temperature is kept at 60°C for 4 hours and the polymer is then deactivated with water.

Two-Block Polymers—TABLE I

Example	Monomer 1	Monomer 2	Amount (g)		Solution of catalyst in THF (ml)	Amount of catalyst (mg)	Yield %	Number-average molecular weight	Elementary analysis			Weight ratio of 1/2 in the copolymer
			1	2					C	H	N	
2	Hexyl methacrylate	N,N-Dimethylaminoethyl methacrylate	135	130	60	2,865(a)	75	36,000(c)	64.0	9.9	6.3	30/70
3	Butyl methacrylate	N,N-Dimethylaminoethyl methacrylate	132	130	60	2,865(a)	85	24,000(c)	63.1	9.9	5.9	34/66
4	Methyl methacrylate	N,N-Dimethylaminoethyl methacrylate	130	130	60	2,865(a)	80	24,000(c)	60.8	9.0	4.1	54/46
5	Styrene	N,N-Dimethylaminoethyl methacrylate	100	50	60	474(b)	76	125,400(c)	82.6	8.4	2.7	69/31
6	Butyl methacrylate	N,N-Dimethylaminoethyl methacrylate	250	150	40	3,820(a)	78	31,600(d)	64.5	9.1	3.6	60/40
7*	N,N-Dimethylaminoethyl methacrylate	Ethylene oxide	50	50	10	955(a)	55					89/11
8**	N,N-Dimethylaminoethyl methacrylate	Octamethylcyclotetrasiloxane	50	50	10	955(a)	63					77/23

Three-Block Polymers—TABLE II

Example	Monomer 1	Monomer 2	Amount (g)		Solution of catalyst in THF (ml)	Amount of catalyst (mg)	Yield %	Number-average molecular weight	Elementary analysis			Weight ratio of 1/2 in the copolymer
			1	2					C	H	N	
9	Butyl methacrylate	N,N-Dimethylaminoethyl methacrylate	70	70	35	2,640(e)	80	31,800(d)	65.9	8.8	4.8	46/54
10	Butyl methacrylate	N,N-Dimethylaminoethyl methacrylate	250	150	200	8,120(f)	75	22,000(d)	64.1	9.4	3.5	60/40
11	Styrene	N,N-Dimethylaminoethyl methacrylate	35	35	20	1,510(e)	85	45,600(d)	76.9	8.9	4.1	54/46
12	N,N-Dimethylaminoethyl methacrylate	Butyl methacrylate	60	140	200	4,060(f)	65	70,000(c)	64.2	9.2	3.8	43/57

Nature of the initiator:

(e): Naphthalene-sodium

(f): 1,1-Diphenylethylene-sodium

Polymers 9 to 11 are of the AAA-BBB-AAA type

Polymer 12 is of the BBB-AAA-BBB type

Nature of the solvent in which the measurement was carried out:

(c) Toluene

(d) Cyclohexanone



Quaternised Polymers—TABLE III

Example	Polymer used		Reactant (g)	% quaternisation or salification	Yield %	Composition of the polymers obtained in g/100 g	
	from Example No.	Weight (g)					
14	3	40	3.2 (a)	15.1	95	Butyl methacrylate 2-N,N-Dimethylamino-ethyl methacrylate Quaternised 2-N,N-dimethylamino-ethyl methacrylate	31.5 51.9 16.6
15	4	40	3.2 (a)	21.7	95	Methyl methacrylate 2-N,N-dimethylamino-ethyl methacrylate Quaternised 2-N,N-dimethylamino-ethyl methacrylate	50.1 33.4 16.6
16	1	40	3.2 (a)	19.2	90	Lauryl methacrylate 2-N,N-dimethylamino-ethyl methacrylate Quaternised 2-N,N-dimethylamino-ethyl methacrylate	51.0 32.4 16.6
17	6	40	3.2 (a)	25	95	Butyl methacrylate 2-N,N-dimethylamino-ethyl methacrylate Quaternised 2-N,N-dimethylamino-ethyl methacrylate	55.6 27.8 16.6
18	9	10	0.8 (a)	18.5	95	Butyl methacrylate 2-N,N-dimethylamino-ethyl methacrylate Quaternised 2-N,N-dimethylamino-ethyl methacrylate	42.6 40.8 16.6
19	9	10	0.79(b)	18.5	90	Butyl methacrylate 2-N,N-dimethylamino-ethyl methacrylate Quaternised 2-N,N-dimethylamino-ethyl methacrylate	42.6 40.8 16.6

Quaternised Polymers—TABLE III (Continued)

Example	Polymer used		Reactant (g)	% quaternisation or salification	Yield %	Composition of the polymers obtained in g/100 g
	from Example No.	Weight (g)				
20	9	10	0.69(c)	18.5	90	Butyl methacrylate 2-N,N-dimethylamino-ethyl methacrylate Quaternised 2-N,N-dimethylamino-ethyl methacrylate
21	10	40	0.8 (a)	25	95	Butyl methacrylate 2-N,N-dimethylamino-ethyl methacrylate Quaternised 2-N,N-dimethylamino-ethyl methacrylate
22	9	10	0.46(d)	37	96	Butyl methacrylate 2-N,N-dimethylamino-ethyl methacrylate Salified 2-N,N-dimethylamino-ethyl methacrylate
23	9	10	1.14(e)	37	95	Butyl methacrylate 2-N,N-dimethylamino-ethyl methacrylate Salified 2-N,N-dimethylamino-ethyl methacrylate

Nature of the quaternising or salifying agent

- (a) : dimethyl sulphate  
 (b) :  $\beta$ -bromoethanol  
 (c) : ethyl bromide  
 (d) : hydrochloric acid  
 (e) : lactic acid

43  
41.2  
15.8  
55.6  
27.8  
16.6  
44  
32.5  
23.5  
41.3  
30.5  
28.2

## COMPOSITION EXAMPLES.

## EXAMPLE A.

A hair wave-setting lotion is prepared, according to the invention, by mixing the following ingredients:

5	Block polymer prepared according to any of Examples 1, 2, 3, 7, 8, 13, 14, 16, 17, 19, 20, 21, 22 or 23	2 g	5
	Ethyl alcohol	50 g	
	Water, q.s.p.	100 g	

10 After applying this lotion to the head of hair, the hair is rolled up on wave-setting  
curlers and dried under a hood. This gives an excellent wave-set, and the hair is  
supple and pleasant to the touch. 10

## EXAMPLE B.

A hair lacquer is prepared, according to the invention, by mixing the following ingredients:

15	Block polymer prepared according to any of Examples 1, 2, 3, 4, 5, 11, 12, 13, 14, 16, 17, 18 or 21	8 g	15
	Ethyl alcohol, q.s.p.	100 g	

25 g of this solution are packaged in an aerosol container with 45 g of trichloro-  
fluoromethane and 30 g of dichlorodifluoromethane.

20 EXAMPLE C. 20  
A hair lacquer is prepared according to the invention by mixing the following ingredients:

25	Two-block polymer prepared according to Example 1	2 g	
	Trichlorofluoromethane	45 g	
	Dichlorodifluoromethane	40 g	25

## EXAMPLE D.

A hair wave-setting lotion is prepared, according to the invention, by mixing the following ingredients:

30	Two-block polymer prepared according to any of Examples 2, 3, 4, 13 or 14	2 g	30
	Ethyl alcohol	50 g	
	Water, q.s.p.	100 g	

35 After the head of hair has been shampooed, the hair is rinsed and the lotion is  
applied uniformly. The hair is then rolled up on wave-setting curlers and dried. This  
gives attractive curls which stay in very well. 35

## EXAMPLE E.

A hair lacquer is prepared, according to the invention, by mixing the following ingredients:

40	Two-block polymer prepared according to any of Examples 2, 3, 4, 13 or 14	8 g	40
	Isopropyl alcohol, q.s.p.	100 g	

25 g of this solution are packaged in an aerosol container with 45 g of trichloro-  
fluoromethane and 30 g of dichlorodifluoromethane.

## EXAMPLE F.

45 A hair wave-setting lotion is prepared, according to the invention, by mixing the  
following ingredients: 45

	Two-block polymer prepared according to Example 14	2 g	
	Isopropyl alcohol	50 g	
	Water, q.s.p.	100 g	

## EXAMPLE G.

A hair wave-setting lotion is prepared, according to the invention, by mixing the following ingredients:

5	Two-block polymer prepared according to Example 16	2 g	
	Ethyl alcohol	50 g	
	Perfume	0.1 g	5
	Water q.s.p.	100 g	

Immediately after rinsing the hair which has been shampooed, the lotion is applied over the entire head of hair. The hair is then rolled up on wave-setting rollers and is dried for 15 minutes. The wave-set obtained holds well and the hair is glossy and soft to the touch. 10

## EXAMPLE H.

A hair lacquer corresponding to the following formulation is prepared:

15	Two-block polymer prepared according to any of Examples 2, 3, 4, 13 or 14	2 g	
	Trichlorofluoromethane	45 g	
	Dichlorodifluoromethane	40 g	15

## EXAMPLE I.

A hair lacquer is prepared in the following manner:  
The following ingredients are mixed:

20	Two-block polymer prepared according to Example 15	8 g	
	Ethyl alcohol, q.s.p.	100 g	20

25 g of the solution obtained are introduced into an aerosol container together with 45 g of trichlorofluoromethane and 30 g of dichlorodifluoromethane.

## EXAMPLE J.

A hair lacquer is prepared as in Example H.

25	Polymer prepared according to any of Examples 1, 2, 3, 5, 11, 13, 16, 17 or 21	2 g	
30	Trichlorofluoromethane	59 g	
	Dichlorodifluoromethane	39 g	30

## EXAMPLE K.

A hair lacquer is prepared in the following manner:

35	Polymer prepared according to Example 5 or 11	2 g	
	Isopropyl alcohol	23 g	
	Trichlorofluoromethane	45 g	
	Dichlorodifluoromethane	30 g	35

## EXAMPLE L.

A hair lacquer is prepared in the following manner:

40	Polymer prepared according to Example 17	1.25 g	
	Ethyl alcohol	48.75 g	
	Nitrous oxide (5 bars)	2 g	40

## EXAMPLE M.

A hair lacquer is prepared in the following manner:

45	Polymer prepared according to Example 21	1 g	
	Ethyl alcohol	49 g	
	Carbon dioxide gas (5 bars)	2 g	45

## EXAMPLE N.

A hair lacquer is prepared in the following manner:

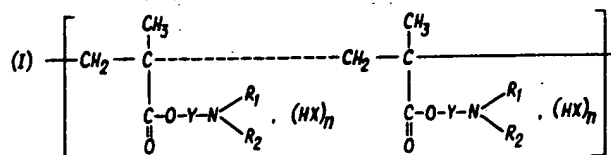
Polymer prepared according to Example 21  
Isopropyl alcohol  
Carbon dioxide gas (5 bars)

1 g  
49 g  
1.6 g

5

## WHAT WE CLAIM IS:—

1. A composition suitable for application to hair, which is oil-free and comprises an acceptable cosmetic vehicle, and at least one two-block or three-block copolymer containing at least one block (A) corresponding to the formula



10

in which:

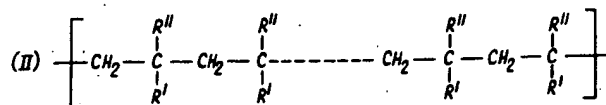
Y represents a saturated hydrocarbon chain of 2 to 4 carbon atoms, or a hydrocarbon chain of 2 to 4 carbon atoms, interrupted by one or more hetero-atoms;

R<sub>1</sub> and R<sub>2</sub>, which may be identical or different, each represents an alkyl radical of 1 to 4 carbon atoms;

each n is 0 or 1,

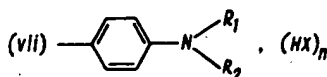
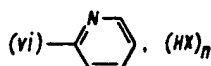
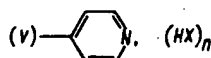
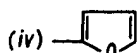
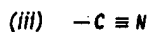
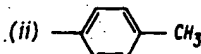
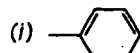
HX represents hydrochloric acid, hydrobromic acid, lactic acid or acetic acid, and, if any n is 0, the corresponding tertiary amine group is optionally quaternised, and at least one block (B) resulting from the polymerisation of an anionically polymerisable monomer.

2. A composition according to claim 1, in which block (B) corresponds to the formula

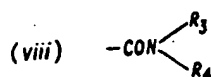


in which:

R' represents



in which case R'' represents a hydrogen atom, or

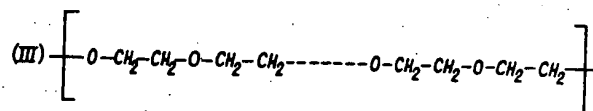


which is optionally partially or completely neutralised by an inorganic or organic base or partially or completely in the form of a sodium, potassium or magnesium salt,

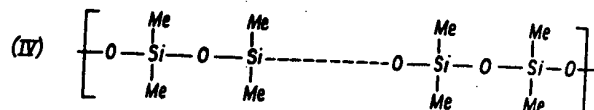
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in which case R'' represents a methyl radical, R<sub>1</sub>, R<sub>2</sub>, n and HX are as defined in claim 1, R<sub>3</sub> represents an alkyl radical of 6 to 18 carbon atoms, R<sub>4</sub> represents a methyl or ethyl radical and R<sub>5</sub> represents an alkyl radical of 1 to 18 carbon atoms.

3. A composition according to claim 1, in which block (B) corresponds to the formula:



4. A composition according to claim 1, in which block (B) corresponds to the formula:



5. A composition according to claim 2, in which block (B) results from the polymerisation of styrene, 4-methyl-styrene, 2-vinyl-pyridine, its hydrochloride or lactate, 4-vinyl-pyridine, its hydrochloride or lactate, *para*-dimethylamino-styrene, its hydrochloride or lactate, methyl methacrylate, ethyl methacrylate, butyl methacrylate, hexyl methacrylate, octyl methacrylate, lauryl methacrylate, stearyl methacrylate, methacrylonitrile, 2-vinyl-furane or N-methyl-N-lauryl-methacrylamide.

6. A composition according to claim 2, in which R' represents —COOH which has been neutralised by ammonia, mono-ethanolamine, diethanolamine, triethanolamine, an isopropanolamine, morpholine, 2-amino-2-methyl-1-propanol or 2-amino-2-methyl-1,3-propanediol.

7. A composition according to any one of the preceding claims in which the hetero-atom(s) in Y is sulphur or oxygen.

8. A composition according to any one of the preceding claims in which block (A) results from the polymerisation of 2-(N,N-dimethylamino)-ethyl methacrylate, 2-(N,N-diethylamino)-ethyl methacrylate, 2-[(2'-N,N-dimethylamino)-ethoxy]-ethyl methacrylate or 2-[2'-(N,N-diethylamino)-ethoxy]-ethyl methacrylate.

9. A composition according to claim 8, in which if n=0 in block (A), the tertiary amine groups are partially or completely quaternised.

10. A composition according to claim 9, in which the tertiary amine groups have been quaternised by dimethyl sulphate, ethyl bromide or β-bromoethanol.

11. A composition according to any one of the preceding claims, in which the polymer has a molecular weight of from 1,000 to 1,000,000.

12. A composition according to claim 11, in which the co-polymer has a molecular weight of from 2,000 to 300,000.

13. A composition according to any one of the preceding claims in which the co-polymer is one specifically identified herein.

14. A composition according to any one of the preceding claims which is in the form of an aerosol lacquer and contains from 0.2 to 5% by weight of said co-polymer, from 0 to 35% by weight of an alcohol and from 60 to 99.8% by weight of a liquefied propellant gas under pressure.

15. A composition according to claim 14 which contains from 0 to 25% by weight of alcohol.

16. A composition according to any one of claims 1 to 13, which is in the form of a wave-setting lotion and contains from 0.2 to 10% by weight of said co-polymer in an aqueous solution or an aqueous-alcoholic solution containing up to 60% by weight of alcohol.

17. A composition according to any one of the preceding claims, which contains at least one of a perfume, dyestuff, preservative, plasticiser, thickener, anionic, cationic or non-ionic surface-active agent, silicone or other cosmetic resin.

18. A composition according to claim 1 substantially as hereinbefore described.

19. A composition according to claim 1, substantially as described in any one of Examples A to N.

20. Process for setting a head of hair which comprises applying thereto a composition as claimed in claim 16 rolling the hair upon wave-setting rollers and drying the hair with external application of heat for 3 to 20 minutes.

21. Process according to claim 20, in which the composition is applied immediately after rinsing shampooed hair.
22. Process according to claim 20 substantially as hereinbefore described.

J. A. KEMP & CO.,  
Chartered Patent Agents,  
14, South Square,  
Gray's Inn,  
London, W.C.1.

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